



A Honeywell Company

## Elemental Composition of Zeolites by ICP-OES

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### UOP Method 961-12

#### Scope

This method is for the determination of components in zeolites by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), following either a digestion or a fusion preparation. Ordinarily, the metals determined include aluminum (Al), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), antimony (Sb), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr). Barium (Ba) and lead (Pb) cannot be determined in the digest due to the formation of insoluble sulfates. Barium can be determined from the fusion solution with a quantitation limit of approximately 0.01 mass-%. This method is suitable for samples containing less than 40 mass-% alumina ( $\text{Al}_2\text{O}_3$ ) and less than 65 mass-% silica ( $\text{SiO}_2$ ); however, it can be readily expanded to samples with other silica/alumina ratios utilizing the same approach as described herein. Zirconium (Zr) at levels above about one mass-% can interfere with the analysis for aluminum when using some instruments, unless an alternative wavelength is used. Precision is about 1 to 2% relative standard deviation for elements present at concentrations greater than 0.1 mass-%. Mass balances between 98.5 and 101.5 mass-% are reported on a volatile-free basis. Precision below 0.1 mass-% does not exceed 10% relative down to the quantitation limits listed in Table 1.

#### References

UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," [www.astm.org](http://www.astm.org)

UOP Method 999, "Precision Statements in UOP Methods," [www.astm.org](http://www.astm.org)

#### Outline of Method

The elements of interest are determined utilizing two dissolution techniques. For Si and Al, a portion of the zeolite sample is fused with lithium tetraborate and the resulting melt is dissolved in 5% hydrochloric acid. The resulting solution is analyzed by ICP and the concentrations of Si and Al are determined by comparison to a NIST standard prepared in the same manner as the samples. The other components are determined following a digestion with sulfuric and hydrofluoric acids. The resulting solution is analyzed by ICP and the concentrations of metals are determined by comparison

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| IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE). |
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to a standard solution of similar elemental and sulfuric acid concentrations. Results are reported on a volatile-free basis, with the loss on ignition (LOI) determined at 900°C by UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents."

**Table 1**  
**Lower Quantitation Limits for Elements**

| <b><u>Element</u></b> | <b><u>Quantitation limits,<br/>µg/mL in solution</u></b> | <b><u>Approximate mass-%<br/>in solid as element</u></b> |
|-----------------------|----------------------------------------------------------|----------------------------------------------------------|
| Al                    | 0.2                                                      | 0.008                                                    |
| Ca                    | 0.1                                                      | 0.004                                                    |
| Co                    | 0.1                                                      | 0.004                                                    |
| Cr                    | 0.1                                                      | 0.004                                                    |
| Cu                    | 0.1                                                      | 0.004                                                    |
| Fe                    | 0.1                                                      | 0.004                                                    |
| Ga                    | 0.2                                                      | 0.008                                                    |
| K                     | 0.2                                                      | 0.008                                                    |
| Li                    | 0.2                                                      | 0.008                                                    |
| Mg                    | 0.1                                                      | 0.004                                                    |
| Mn                    | 0.1                                                      | 0.004                                                    |
| Mo                    | 0.2                                                      | 0.008                                                    |
| Na                    | 0.2                                                      | 0.008                                                    |
| Ni                    | 0.1                                                      | 0.004                                                    |
| P                     | 0.4                                                      | 0.016                                                    |
| Sb                    | 0.2                                                      | 0.008                                                    |
| Si                    | 0.4                                                      | 0.016                                                    |
| Sn                    | 0.2                                                      | 0.008                                                    |
| Sr                    | 1.0                                                      | 0.040                                                    |
| Ti                    | 0.1                                                      | 0.004                                                    |
| V                     | 0.1                                                      | 0.004                                                    |
| Zn                    | 0.1                                                      | 0.004                                                    |
| Zr                    | 0.1                                                      | 0.004                                                    |

## Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

*Balance*, readable to 0.0001 g

*Balance*, top-loading, readable to 0.01 g

*Beaker*, quartz, 250-mL, Ace Glass, Cat. No. 5334-14

*Beaker*, PTFE, 100- and 250-mL, Fisher Scientific, Cat. Nos. 02-586-1G and -1H, respectively

*Bottles*, 500-mL, wide mouth, FEP, Fisher Scientific, Cat. No. 02-924-15E, several required

*Bottle*, washing, one-liter, polypropylene, Fisher Scientific, Cat. No. 03-409-14C

*Burner*, blast, VWR Scientific, Cat. No. 89038-548

*Crucible*, high form, platinum, 25-mL, Cole Parmer, Cat. No. EW-17830-45

*Cylinder*, graduated, polypropylene, 10-mL, Fisher Scientific, Cat. No. 03-007-38

*Cylinders*, graduated, 50- and 100-mL, Fisher Scientific, Cat. Nos. 08-552-4B and -4C, respectively

*Flasks*, volumetric, Class A, 500- and 2000-mL, Fisher Scientific, Cat. Nos. 10-210F, and -210H, respectively, several of each required

*Flasks*, volumetric, 100- and 500-mL, PMP, Fisher Scientific, Cat. Nos. 10-198-52C and -52F, respectively

*Flasks*, volumetric, 100-mL, polypropylene, Fisher Scientific, Cat. No. 10-198-50B

*Funnel*, 55-mm diameter, Fisher Scientific, Cat. No. 10-371H

*Fluxer*, Claisse (optional), with necessary crucibles and other equipment, Claisse, Model Fluxy-30; replacement crucible, Cat. No. P-130-00

*Hot plate*, stirring, variable heat, Fisher Scientific, Cat. No. 11-300-49SHP

*Hot plate*, variable heat, Corning Model PC-600, Fisher Scientific, Cat. No. 11-100-49H

*Inductively Coupled Plasma-Optical Emission Spectrometer* (ICP-OES), Perkin-Elmer Optima 8300DV

*Mortar and pestle*, agate, Fisher Scientific, Cat. No. 12-950B

*Muffle furnace* (optional), capable of 1000°C. The interior surface of the furnace must be of non-flaking material or sample contamination may result.

*Oven*, drying, capable of 105°C

*Pipets*, total volume, Class A, 5-, 10-, 15-, 20-, and 25-mL, Fisher Scientific, Cat. Nos. 13-650-2F, -2L, -2M, -2N, and -2P, respectively, several of each required

*Regulator*, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

*Stir bar*, magnetic, PTFE coated, 3 x 13-mm, Fisher Scientific, Cat. No. 14-513-57

*Tongs*, crucible, stainless steel, lock joint, platinum shoes, Fisher Scientific, Cat. No. 15-205

*Triangle*, nickel-chromium, 2-inch (51-mm), Fisher Scientific, Cat. No. 15-260B

*Vacuum Desiccator*, Corning No. 3118-160, Fisher Scientific, Cat. No. 08-632

*Watch glass*, borosilicate glass, 90-mm diameter, Fisher Scientific, Cat. No. 02-612C

*Watch glass*, PTFE, 100-mm, Fisher Scientific, Cat. No. 02-610-5E

## Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized water.

*Argon*, 99.995% minimum purity, plasma and nebulizer gas

*Gloves*, nitrile, Fisher Scientific, Cat. No. 11-393-64A through -64E, corresponding to hand sizes 7 through 11

*Hydrochloric acid*, concentrated, trace metal grade, Fisher Scientific, Cat. No. A508SK212

*Hydrochloric acid*, 5% (vol/vol). Fill a 2000-mL flask approximately ½ full with water. Add 100 mL of concentrated hydrochloric acid and dilute to the mark with water.

*Hydrofluoric acid*, concentrated, trace metal grade, Fisher Scientific, Cat. No. A513-500

*Lithium tetraborate*, Ultra Pure, SPEX CertiPrep, Cat. No. FF-0601

*Nitric acid*, concentrated

*Nitrogen*, 99.99% minimum purity, water and oil free, ICP optics purge gas

*Scandium oxide*, 99.998% (metals basis), VWR, Cat. No. 10916

*Scandium solution*, 500-µg/mL. Weigh  $1.534 \pm 0.001$  g into a 250-mL quartz beaker, rinse inside walls with water, and add an additional 20 mL of water. Add 50 mL of concentrated hydrochloric acid. Cover with a watch glass, and place on a hot plate set at 200°C until dissolved. Cool and quantitatively transfer with water into a 2000-mL volumetric flask. Bring to volume with water. Store in four 500-mL FEP plastic bottles.

*Scandium solution*, 100-µg/mL. Pipet 100 mL of the 500-µg/mL scandium solution into a 500-mL volumetric flask. Bring to volume with water.

*Soda feldspar*, National Institute of Standards and Technology (NIST), Cat. No. 99b

*Standard solutions of metals*, see Table 2, SPEX CertiPrep

*Water*, deionized

**Table 2**

| Concentration, |              |                 | Concentration, |              |                 |
|----------------|--------------|-----------------|----------------|--------------|-----------------|
| <u>Metal</u>   | <u>µg/mL</u> | <u>Cat. No.</u> | <u>Metal</u>   | <u>µg/mL</u> | <u>Cat. No.</u> |
| Al             | 10,000       | PLAL1-3X        | Mo             | 10,000       | PLMO9-3X        |
| Ca             | 10,000       | PLCA1-3X        | Na             | 10,000       | PLNA1-3X        |
| Co             | 10,000       | PLCO2-3X        | Ni             | 10,000       | PLNI2-3X        |
| Cr             | 10,000       | PLCR1-3X        | P              | 10,000       | PLP9-3X         |
| Cu             | 10,000       | PLCU1-3X        | Sb             | 1,000        | PLSB5-2X        |
| Fe             | 10,000       | PLFE1-3X        | Sn             | 1,000        | PLSN5-2X        |
| Ga             | 1,000        | PLGA2-2X        | Sr             | 1,000        | PLSR2-2X        |
| K              | 10,000       | PLK1-3X         | Ti             | 10,000       | PLTI5-3X        |
| Li             | 1,000        | PLLI2-2X        | V              | 10,000       | PLV3-3X         |
| Mg             | 10,000       | PLMG1-3X        | Zn             | 10,000       | PLZN2-3X        |
| Mn             | 10,000       | PLMN2-3X        | Zr             | 10,000       | PLZR3-3X        |

## Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ICP-OES, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

**CAUTION:** All subsequent steps involving lithium tetraborate fusion and handling of concentrated acids must be performed in a properly operating fume hood, and appropriate personal protection equipment must be worn (see the MSDS for each material used).

## Preparation of ICP Calibration Standards and Blanks

Scandium is used as an internal standard; other elements and/or concentrations can be utilized; adjust accordingly (see *Note*). Label and date all standard and blank solution containers.

### ***Lithium Tetraborate Calibration Standard for Aluminum and Silicon***

A solution of fused NIST 99b is used to calibrate the ICP for the determination of aluminum and silicon. This is used because of difficulties encountered with the accuracy and stability of commercial aqueous silicon standards.

1. Dry a portion of NIST 99b in an oven at 105°C for 2 hours, remove and place in a desiccator to cool.
2. Weigh  $0.15 \pm 0.01$  g, to the nearest 0.0001 g, of dried NIST 99b into a platinum crucible.
3. Weigh  $1.50 \pm 0.02$  g, to the nearest 0.01 g, of lithium tetraborate into the platinum crucible, using a top-loading balance. Rotate and tilt the crucible by hand to mix the material with the lithium tetraborate flux.
4. Place the crucible on a triangle and heat with a blast burner for a minimum of 30 minutes, occasionally checking for unfused material as evidenced by white specks in the melt. The fusion is complete when the melt is entirely clear. The fusion can also be performed in a muffle furnace set at 1000°C, or by using an automated fusion apparatus (fluxer).
  - If unfused sample is detected, mix the hot melt by rotating and tilting the hot crucible with tongs, and continuing fusion until it is complete.
5. Remove the crucible from the flame using the platinum tipped tongs, place it upright in a 250-mL quartz beaker and allow to cool for about 5 minutes.
6. Place a stir bar inside the crucible and add 5% hydrochloric acid so that the crucible is submerged by about 10 mm.
7. Cover the beaker with a watch glass and place it on a stirring hot plate. Adjust the heat to achieve mild boiling and the stirrer to achieve a vortex in the solution.
8. Continue heating until the fusion melt has completely dissolved, usually within 10 minutes after boiling begins.
  - Carefully check the crucible and the beaker for any particulates, indicating undissolved NIST 99b. If any doubt remains as to the completeness of the fusion or dissolution of the melt, discard the solution and start over at Step 1.
9. Remove the beaker from the hot plate and allow it to cool. Using the 5% hydrochloric acid from the wash bottle and a funnel, quantitatively transfer the beaker contents into a 500-mL volumetric flask.
  - The crucible is to remain in the beaker. Use the wash bottle to wash the interior and exterior walls of the crucible as well as the beaker walls during transfer.
10. Pipet 2 mL of the 500-µg/mL scandium solution into the volumetric flask.
11. Allow the solution to cool to ambient temperature and then dilute to the mark with 5% hydrochloric acid. Stopper and invert several times to mix thoroughly and then transfer the solution to a labeled and dated 500-mL FEP bottle for storage.
12. Calculate the aluminum and silicon concentrations using Equation 1:

$$\text{Si or Al Concentration, } \mu\text{g/mL} = 10,000 \frac{CW}{500} \quad (1)$$

where:

**C** = certified value for Si or Al in NIST 99b, mass-%

**W** = mass of dried NIST 99b taken (Step 2), g

**500** = volumetric flask volume, mL

**10,000** = factor to convert mass-% to µg/g

13. Calibrate the ICP with the new NIST 99b standard solution as described in *Sample Analysis* and compare to the old, previously utilized standard solution. The results should agree within 2% (relative) of certified values.
  - For the initial establishment of a calibration curve, also fuse and analyze a portion of NIST 99b as an unknown. The values should be within 2% relative of the certified values. If the values returned for the unknown NIST 99b portion are too low, the fusion of the unknown portion was incomplete. If the values are too high, the fusion for the calibration standard was incomplete.

### ***Lithium Tetraborate Calibration Standard Blank***

1. Weigh  $1.50 \pm 0.02$  g, to the nearest 0.01 g, of lithium tetraborate into a 500-mL volumetric flask.
2. Add approximately 100 mL of 5% hydrochloric acid to dissolve the powder. Heat on a hot plate set at 200°C until dissolved.
3. Pipet 2 mL of 500-µg/mL scandium solution into the volumetric flask.
4. Allow the solution to cool to ambient temperature and dilute to the mark with 5% hydrochloric acid. Stopper and invert several times to mix thoroughly and then transfer the solution to a labeled and dated 500-mL FEP bottle for storage.
  - The calibration standard and blank are stable for three months.
  - Make up new calibration solutions when the ones in use are about 75% consumed or are older than three months.
  - A blank is necessary due to trace levels of silicon and aluminum found in commercial batches of lithium tetraborate and for matrix matching. This blank is also to be used for diluting samples where the Al or Si concentration is above the concentration in the NIST 99b standard calibration solution.
  - Because of varying contamination levels, the blank and calibration solutions are to be made using the same lot of lithium tetraborate.
  - When starting to use a new lot of lithium tetraborate, make up a new calibration standard and blank.

### ***Calibration Stock Solutions***

1. Prepare 500 mL of each of the three calibration stock solutions by pipetting the volumes of the element concentrate solutions indicated in Table 3 into 500-mL PMP volumetric flasks.
2. Using a graduated cylinder, add 25 mL of concentrated hydrochloric acid to each flask, then carefully add water to fill the flasks half full and swirl to mix the contents.
3. Add 5 mL of concentrated hydrofluoric acid to calibration solution 2 only.
4. Allow to cool, fill to mark with water, stopper and invert to mix.
  - Make a new calibration stock solution when approximately 75% of the old one has been consumed or it is three months old.
5. Transfer to a 500-mL wide mouth FEP bottle and label the contents.

Prepare three calibration standards from the stock solutions as follows:

1. Into each of three 100-mL polypropylene volumetric flasks, pipet 20 mL of the respective stock solutions. Use a fourth 100-mL polypropylene volumetric flask as a blank.
2. Match the level of the alumina in the standards to the concentration in the samples. Pipet an amount of the 10,000-µg/mL aluminum single element standard to match the concentration in the sample into each of the four volumetric flasks.

- If the alumina concentration is unknown, analyze the sample digest by preparing a calibration standard solution of 1000- $\mu\text{g/mL}$  aluminum, 2- $\mu\text{g/mL}$  scandium, and the acids as described herein, and by analyzing the digest against this standard.
3. Using a graduated cylinder, add 4 mL of sulfuric acid to the volumetric flasks.
  4. Using a pipet, add 2.0 mL of 100  $\mu\text{g/mL}$  scandium single element standard solution to the flasks. Fill to the mark with water. Cap and mix by inverting several times.
  5. Label the volumetric flasks as containing each of the elements added at 1/5 of the concentration of the Stock Solution, 2- $\mu\text{g/mL}$  scandium, and indicate the concentration of aluminum. Calibration standards should be discarded after one month.
    - Different concentrations of calibration standards may be prepared as needed by varying the amount of the stock solution added.

Since the response of the ICP-OES is linear within the defined range of quantitation, single point standards are used.

**Table 3**  
**Calibration Stock Solution Volumes and Concentrations**

| <b>Element</b>                       | <b>Volume, mL</b> | <b>Element in Concentrate, <math>\mu\text{g/mL}</math></b> | <b>Element Concentration in the Calibration Stock Solution, <math>\mu\text{g/mL}</math></b> |
|--------------------------------------|-------------------|------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| <b><u>Calibration Solution 1</u></b> |                   |                                                            |                                                                                             |
| Ca                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Co                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Cr                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Cu                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Fe                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Ga                                   | 50                | 1,000                                                      | 100                                                                                         |
| K                                    | 5                 | 10,000                                                     | 100                                                                                         |
| Li                                   | 50                | 1,000                                                      | 100                                                                                         |
| Mg                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Mn                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Na                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Ni                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Sr                                   | 10                | 1,000                                                      | 20                                                                                          |
| V                                    | 5                 | 10,000                                                     | 100                                                                                         |
| Zn                                   | 5                 | 10,000                                                     | 100                                                                                         |
| <b><u>Calibration Solution 2</u></b> |                   |                                                            |                                                                                             |
| Mo                                   | 5                 | 10,000                                                     | 100                                                                                         |
| P                                    | 10                | 10,000                                                     | 200                                                                                         |
| Ti                                   | 5                 | 10,000                                                     | 100                                                                                         |
| Zr                                   | 10                | 10,000                                                     | 200                                                                                         |
| <b><u>Calibration Solution 3</u></b> |                   |                                                            |                                                                                             |
| Sb                                   | 50                | 1,000                                                      | 100                                                                                         |
| Sn                                   | 50                | 1,000                                                      | 100                                                                                         |

### Sample Preparation

Samples are generally provided in powder form; but if provided as pill (sphere) or extrudate, they must be ground. A mortar and pestle or any commercial grinding apparatus may be used.

#### ***Lithium Tetraborate Fusion***

1. Weigh  $0.10$  to  $0.12 \pm 0.01$  g of powder sample, to the nearest  $0.0001$  g, into a platinum crucible.
2. Weigh  $1.5 \pm 0.02$  g of lithium tetraborate, to the nearest  $0.01$  g, into the crucible. Rotate and tilt the crucible by hand to mix the sample with the lithium tetraborate.
3. Weigh a sample portion for LOI at  $900^{\circ}\text{C}$  (or other temperature appropriate to the sample being run) by UOP Method 954 at the same time the sample is weighed for the metal determinations.
4. Fuse the sample in the same manner as described in Steps 4 – 11 of *Lithium Tetraborate Calibration Standard for Aluminum and Silicon*.

#### ***Sulfuric/Hydrofluoric Acid Digestion***

1. Weigh  $0.25 \pm 0.05$  g of powder sample, to the nearest  $0.0001$  g, into a 250-mL PTFE beaker.
2. Wet the contents with water and then add an additional 20 mL of water.
3. Using a graduated cylinder, add  $4.0 \pm 0.1$  mL of sulfuric acid and swirl to mix.
4. Using a polypropylene graduated cylinder, add 2 to 3 mL of hydrofluoric acid.
5. Place the uncovered beaker on a hot plate and heat until white fumes of sulfuric acid appear.
  - Do not overheat as evaporation of sulfuric acid will make the matrix matching problematic.
6. Remove the beaker from the hot plate and allow it to cool. Check to see if the contents are dark-colored due to the presence of organic materials or coke that may have been in the sample. If dark, add approximately 2 mL of concentrated nitric acid and place the beaker back on the hot plate until white fumes of sulfuric acid evolve and the solution is no longer dark (repeat the addition of nitric acid if required). Remove the beaker from the hot plate and allow it to cool.
  - Do not overheat as evaporation of sulfuric acid will make the matrix matching problematic.
7. Add slowly, about 40 mL of water to the sample, cover the beaker with a PTFE watch glass and return it to the hot plate. Let the sample boil until the solution is clear, remove and allow to cool.
8. Transfer quantitatively, the contents of the beaker into a 100-mL PMP volumetric flask. Pipet 2 mL of 100- $\mu\text{g/mL}$  scandium solution into the flask.
9. Allow to cool to ambient temperature and fill to the mark with water. Stopper and invert the flask several times to mix.

### Sample Analysis

Set up the ICP-OES instrument in accordance with the manufacturer's guidelines. Table 4 lists the recommended wavelengths for each element (alternative wavelengths are listed in parentheses). Other wavelengths may need to be used because of spectral interference. If the concentration of Al is less than  $0.5 \mu\text{g/mL}$  in the fusion solution (equal to 0.1 mass-% Al or 0.2 mass-%  $\text{Al}_2\text{O}_3$  in the sample), determine the Al concentration from analysis of the sulfuric acid digest.

1. Standardize the instrument by aspirating the blank, followed by the standards.
  - Allow sufficient wash-out time between aspirations.

2. Aspirate the samples, after entering the dilution factors into the computer.
3. Check how well the calibration is holding by aspirating the calibration standards, treating them as unknowns with no dilution factors. Check after every fifth sample, and following the final sample.
  - Any calibration checks and the final standard reading should return the concentrations of the elements in the standards within  $\pm 2\%$  relative. If not, re-calibrate and re-analyze the sample solutions.

**Table 4**  
**Recommended Wavelengths**

| <u>Metal</u> | <u><math>\lambda</math>, nm</u>              | <u>Metal</u> | <u><math>\lambda</math>, nm</u>   | <u>Metal</u>    | <u><math>\lambda</math>, nm</u>   |
|--------------|----------------------------------------------|--------------|-----------------------------------|-----------------|-----------------------------------|
| Al           | 396.152<br>308.210 <sup>a</sup><br>(394.401) | Li           | 610.364<br>(670.788)              | Sc <sup>b</sup> | 424.683                           |
| Ca           | 317.933<br>422.673                           | Mg           | 285.213<br>(280.261)              | Si              | 251.611                           |
| Co           | 228.609<br>(238.892)                         | Mn           | 257.610<br>(260.561)              | Sn              | 189.989<br>(235.484)<br>(283.991) |
| Cr           | 205.552<br>(206.159)                         | Mo           | 202.031<br>(204.595)              | Sr              | 407.775<br>421.563<br>460.739     |
| Cu           | 324.754<br>(224.701)<br>(327.396)            | Na           | 589.592                           | Ti              | 334.941<br>(337.285)              |
| Fe           | 238.204                                      | Ni           | 231.604<br>(232.005)              | V               | 292.402<br>(290.880)              |
| Ga           | 417.214<br>(294.361)                         | P            | 213.618<br>(178.222)<br>(214.909) | Zn              | 213.857<br>206.197                |
| K            | 766.491                                      | Sb           | 206.830<br>217.580                | Zr              | 339.194<br>(343.827)              |

<sup>a</sup>For high zirconium samples

<sup>b</sup>Internal standard

## Calculations

If the dilution factor for the sample is entered into the instrument computer, the concentrations of the elements in the original sample are reported automatically. Round to the nearest 0.01 mass-%, not to exceed three significant figures.

If the LOI value is available prior to the instrument analysis, the sample weight can be corrected for volatile content, the corrected value entered into the instrument computer, and the computer will calculate results on a volatile-free (VF) basis. If the LOI is not available at the time of the analysis, manually calculate the concentration of each element in the original sample on a volatile-free (VF) basis as follows:

$$\text{Concentration, mass - \% VF} = \frac{C}{\left(1 - \frac{D}{100}\right)} \quad (2)$$

where:

**C** = concentration of element on an as-received basis, mass-%

**D** = % LOI as determined by UOP Method 954, mass-%

**1** = factor to convert mass fraction LOI to mass fraction dry solids  
**100** = factor to convert mass-% LOI to mass fraction, mass-%

## Report

Every sample result must be checked for mass balance if an LOI was performed. Use the gravimetric factors listed in Table 5 to convert elemental concentrations to oxides. Report results only when the mass balance is between 98 and 102 mass-%, otherwise rerun the sample. If the mass balance is low, scan the sulfuric acid digest to determine if any missing elements (for example, boron, noble metals, and rare earths) are present. Through the use of appropriate standards, and using the procedures listed herein, determine the amount of any such elements found and include them in the final report.

**Table 5**  
**Gravimetric Conversion Factors**

| <u>To Convert</u>                    | <u>Multiply By</u> | <u>To Convert</u>                    | <u>Multiply By</u> |
|--------------------------------------|--------------------|--------------------------------------|--------------------|
| Al to Al <sub>2</sub> O <sub>3</sub> | 1.89               | Na to Na <sub>2</sub> O              | 1.35               |
| Ca to CaO                            | 1.40               | Ni to NiO                            | 1.27               |
| Co to CoO                            | 1.27               | P to P <sub>2</sub> O <sub>5</sub>   | 2.29               |
| Cr to Cr <sub>2</sub> O <sub>3</sub> | 1.46               | Sb to Sb <sub>2</sub> O <sub>3</sub> | 1.20               |
| Cu to CuO                            | 1.25               | Si to SiO <sub>2</sub>               | 2.14               |
| Fe to Fe <sub>2</sub> O <sub>3</sub> | 1.43               | Sn to SnO <sub>2</sub>               | 1.27               |
| Ga to Ga <sub>2</sub> O <sub>3</sub> | 1.34               | Sr to SrO                            | 1.18               |
| K to K <sub>2</sub> O                | 1.20               | Ti to TiO <sub>2</sub>               | 1.67               |
| Li to Li <sub>2</sub> O              | 2.15               | V to V <sub>2</sub> O <sub>5</sub>   | 1.78               |
| Mg to MgO                            | 1.66               | Zn to ZnO                            | 1.24               |
| Mn to MnO <sub>2</sub>               | 1.58               | Zr to ZrO <sub>2</sub>               | 1.35               |
| Mo to MoO <sub>3</sub>               | 1.50               |                                      |                    |

## Note

Some elements, such as barium, cannot be analyzed by sulfuric acid digestion because of limited solubility. These metals may be measured using the lithium tetraborate preparation or by using additional acids not listed herein. Additional calibration solutions must be prepared.

## Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

### Repeatability and Site Precision

A nested design was carried out for determining metals in zeolites. One sample was analyzed by two analysts, with each analyst performing two analyses on three separate days for a total of 12 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 6. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 6 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 6 with 95% confidence.

The data in Table 6 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

**Table 6**  
**Repeatability and Site Precision, mass-%**

| <u>Element</u> | <u>Mean</u> | <u>Repeatability</u>  |                             | <u>Site Precision</u> |                             |
|----------------|-------------|-----------------------|-----------------------------|-----------------------|-----------------------------|
|                |             | <u>Within-Day esd</u> | <u>Allowable Difference</u> | <u>Within-Lab esd</u> | <u>Allowable Difference</u> |
| Al*            | 15.787      | 0.0740                | 0.256                       | 0.1454                | 0.654                       |
| Ca             | 0.011       | 0.0027                | 0.004                       | 0.0050                | 0.009                       |
| Fe             | 0.314       | 0.0094                | 0.032                       | 0.0142                | 0.064                       |
| K              | 0.070       | 0.0015                | 0.005                       | 0.0019                | 0.007                       |
| Mg             | 0.015       | 0.0005                | 0.002                       | 0.0010                | 0.006                       |
| Na             | 0.048       | 0.0016                | 0.006                       | 0.0016                | 0.006                       |
| P              | 7.156       | 0.0695                | 0.241                       | 0.2020                | 0.909                       |
| Si*            | 20.047      | 0.1238                | 0.428                       | 0.1796                | 0.808                       |
| Ti             | 0.532       | 0.0048                | 0.016                       | 0.0048                | 0.017                       |
| Zr             | 0.006       | 0.0004                | 0.001                       | 0.0007                | 0.003                       |

\*Aluminum and silicon were analyzed using lithium tetraborate fusion. The other elements were analyzed using sulfuric/hydrofluoric acid digestion

### **Reproducibility**

There is insufficient data to calculate the reproducibility of the test at this time.

### **Bias**

The bias of the analysis was determined by analyzing the NIST 99a Standard Reference Material, and the data are listed in Table 7. The values agree within the experimental error of the test. There is no significant bias to the test.

**Table 7**  
**Bias**

| <u>Component</u>               | <u>NIST Certified Values</u> |                    | <u>This Method</u> |                    |
|--------------------------------|------------------------------|--------------------|--------------------|--------------------|
|                                | <u>mass-%</u>                | <u>esd, mass-%</u> | <u>mass-%</u>      | <u>esd, mass-%</u> |
| Al <sub>2</sub> O <sub>3</sub> | 20.5                         | 0.1                | 20.6               | 0.15               |
| SiO <sub>2</sub>               | 65.2                         | 0.1                | 65.2               | 0.53               |
| Na <sub>2</sub> O              | 6.2                          | 0.1                | 6.2                | 0.07               |
| K <sub>2</sub> O               | 5.2                          | 0.1                | 5.3                | 0.06               |
| CaO                            | 2.14                         | 0.01               | 2.1                | 0.04               |

### **Time for Analysis**

The elapsed time for one analysis is 4 hours. The labor requirement is 2 hours.

### **Suggested Suppliers**

Ace Glass, Inc., 1430 North West Blvd., Vineland, NJ 08362-0688, USA (856-691-3333)  
www.aceglass.com

Cole-Parmer, 625 East Bunker Court, Vernon Hills, IL 60061, USA (847-549-7600)  
www.coleparmer.com

Corporation Scientifique Claisse, 350 rue Franquet, Suite 45, Quebec, Canada G1P 4P3 (418-656-6453) [www.claisse.com](http://www.claisse.com)

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300)  
[www.fishersci.com](http://www.fishersci.com)

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA (215-641-2700)  
[www.mathesontrigas.com](http://www.mathesontrigas.com)

National Institute of Standards and Technology (NIST), Standard Reference Materials Group, 100  
Bureau Dr., Gaithersburg, MD 20899, USA (301-975-6776) [www.nist.gov](http://www.nist.gov)

PerkinElmer Analytical Instruments, 710 Bridgeport Ave., Shelton, CT 06484-4794, USA (203-  
925-4600) [www.perkinelmer.com](http://www.perkinelmer.com)

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA (732-549-7144)  
[www.spexcsp.com](http://www.spexcsp.com)

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA (610-431-1700)  
[www.vwr.com](http://www.vwr.com)